PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : A61K 7/42

A1

(11) International Publication Number: WO 94/04131

(43) International Publication Date: 3 March 1994 (03.03.94)

(21) International Application Number: PCT/US93/06897

(22) International Filing Date: 23 July 1993 (23.07.93)

(30) Priority data:
07/929,612 13 August 1992 (13.08.92) US

(71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventor: DECKNER, George, Endel ; 10572 Tanager Hills Drive, Cincinnati, OH 45249 (US).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US).

(81) Designated States: AU, CA, FI, JP, NO, NZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: PHOTOSTABLE SUNSCREEN COMPOSITIONS

(57) Abstract

The present invention relates to sunscreen compositions having improved photostability, especially in the UVA region, along with providing broad coverage in both the UVA and UVB regions. These compositions are achieved by combining a UVA-absorbing dibenzoylmethane sunscreen with a UVB-absorbing benzylidene camphor sunscreen. In highly preferred embodiments, these compositions also contain from about 0.1 % to about 25 % of an inorganic physical sunblock. These compositions are useful for protecting the skin from the harmful effects of ultraviolet radiation and for moisturizing the skin.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic			SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovak Republic
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	UA	Ukraine
DE	Germany	MG	Madagascar	US	United States of America
DK	Denmark	ML	Mali	UZ	Uzbekistan
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

3NSDOCID: <WO___9404131A1_I_>

PHOTOSTABLE SUNSCREEN COMPOSITIONS

TECHNICAL FIELD

The present invention relates to sunscreen compositions having improved photostability, especially in the UVA region, along with providing broad coverage in both the UVA and UVB regions. These compositions are achieved by combining a UVA-absorbing dibenzoylmethane sunscreen with a UVB-absorbing benzylidene camphor sunscreen. In highly preferred embodiments, these compositions also contain from about 0.1% to about 25% of an inorganic physical sunblock. These compositions are useful for protecting the skin from the harmful effects of ultraviolet radiation.

BACKGROUND OF THE INVENTION

The damaging effects of sunlight on skin are well documented. The major short term hazard of prolonged exposure to sunlight is erythema (i.e. sunburn). The 290 to 320 nanometer wavelength ultraviolet radiation range, designated as the "UVB" wavelength range, tends to be the primary cause of erythema. The 320 to 400 nanometer wavelength ultraviolet radiation range, designated as the "UVA" wavelength range, also produces erythema, but much more energy is required.

In addition to the short term hazard of erythema, there are also long term hazards associated with UV radiation exposure. One of these long term hazards is malignant changes in the skin surface. Numerous epidemiologic studies demonstrate a strong relationship between sunlight exposure and human skin cancer.

Another long term hazard of ultraviolet radiation is premature aging of the skin. This condition is characterized by wrinkling and yellowing of the skin, along with other physical changes such as cracking, telangiectasis (spider vessels), solar keratoses (growths), ecchymoses (subcutaneous hemorrhagic lesions), and loss of elasticity (sagging). The

adverse effects associated with exposure to UVA and UVB wavelength radiation are more fully discussed in DeSimone, "Sunscreen and Suntan Products", Handbook of Nonprescription Drugs, 7th Ed., Chapter 26, pp. 499-511 (American Pharmaceutical Association, Washington, D.C.; 1982); Grove and Forbes, "A Method for Evaluating the Photoprotection Action of Sunscreen Agents Against UV-A Radiation", International Journal of Cosmetic Science, 4, pp. 15-24 (1982); and U.S. Patent 4,387,089, to DePolo, issued June 7, 1983; which are all incorporated by reference herein.

Both sunscreen agents and physical sunblocks are commercially available to protect the skin from UV radiation. Without being limited by theory, it is believed that sunscreen agents exert their effects through chemical means, i.e., they absorb ultraviolet radiation so that it cannot penetrate the skin. Physical sunblocks scatter, reflect, and absorb ultraviolet radiation. See, Sayre, R.M. et al., "Physical Sunscreens", J. Soc. Cosmet. Chem., vol. 41, no. 2, pp. 103-109 (1990).

Most commercially-available sunscreen agents are primarily UVB absorbers. The number of UVA absorbers is more limited, with benzophenones and dibenzoylmethanes being the most well-known. U.S. Patent No. 4,489,057, to Welters et al., issued December 18, 1984, and U.S. Patent No. 4,387,089, to DePolo, issued June 7, 1983 both disclose dibenzoylmethane sunscreen agents. However, despite their highly desirable UVA absorption, dibenzoylmethane sunscreen agents tend to photodegrade during UV exposure, thereby reducing their effectiveness.

Previous researchers have attempted to overcome this photostability problem of dibenzoylmethanes. For example, British Patent GB 2,198,944, to Dellandre et al., published June 29, 1988, teaches photostable sunscreen compositions having at least a 3:1 ratio of the sunscreen 3-(4-methylbenzylidene)camphor to 4,4'-methoxy-t-butyl-

dibenzoylmethane. However, this combination has the disadvantage of requiring more of the camphor derivative relative to the dibenzoylmethane than may be needed or desired, thus resulting in an imbalance of UVA to UVB protection and in formulation constraints.

In the present invention, it has been found that dibenzoylmethane containing compositions having improved photostability can be prepared by utilizing about a 1:1 ratio of a dibenzoylmethane sunscreen to a benzylidene camphor sunscreen. In highly preferred embodiments, these compositions also contain an inorganic physical sunblock, which in even further embodiments can be surface treated.

It is therefore an object of the present invention to provide sunscreen compositions having improved photostability, especially in the UVA region.

It is another object of the present invention to provide photostable sunscreen compositions which will prevent both acute effects (e.g., erythema) and chronic effects (e.g. photoaging and skin cancer) of exposure to sunlight and other sources of UV radiation.

It is a further object of the present invention to provide photostable sunscreen compositions which are not readily absorbed by the skin; which have a decreased chance for allergy, irritation, or toxicity problems resulting from daily or almost daily use; which are less susceptible to rub off; and which are cosmetically acceptable.

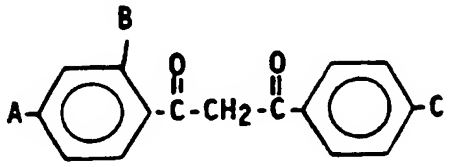
It is an even further object of the present invention to provide photostable sunscreen compositions which are suitable for daily use and which also moisturize the skin.

These and other objects will become readily apparent from the detailed description which follows.

SUMMARY OF THE INVENTION

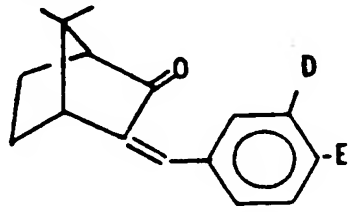
The present invention relates to a sunscreen composition having improved photostability and broad UVA and UVB coverage, comprising:

(a) from about 0.1% to about 10% of a sunscreen compound (I) having the general structure



wherein A is a substituent selected from the group consisting of H, -OR, and $-NR_2$ wherein each R is independently H, or straight or branched chain alkyl having from about 1 to about 20 carbon atoms; B is a substituent selected from the group consisting of H and -OH; and C is a substituent selected from the group consisting of H, or straight or branched chain alkyl having from about 1 to about 20 carbon atoms;

(b) from about 0.1% to about 10% of a sunscreen compound (II) having the general structure



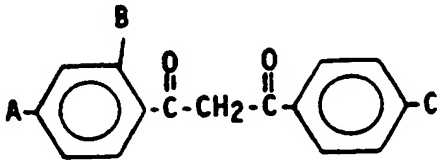
wherein D and E are substituents independently selected from the group consisting of H, straight or branched chain alkyl having from about 1 to about 20 carbon atoms, and -OR, wherein R is H or straight or branched chain alkyl having from about 1 to about 20 carbon atoms; and

(c) a pharmaceutically-acceptable carrier;

wherein the weight ratio of sunscreen compound (I) to sunscreen compound (II) is from about 1:1.5 to about 1.5:1.

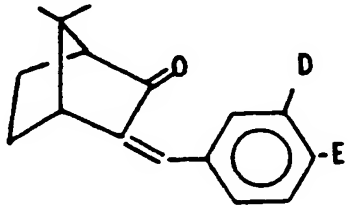
In further embodiments the present invention relates to a sunscreen composition having improved photostability and broad UVA and UVB coverage, comprising:

(a) from about 0.1% to about 10% of a sunscreen compound (I) having the general structure



wherein A is a substituent selected from the group consisting of H, -OR, and $-NR_2$ wherein each R is independently H, or straight or branched chain alkyl having from about 1 to about 20 carbon atoms; B is a substituent selected from the group consisting of H and -OH; and C is a substituent selected from the group consisting of H, or straight or branched chain alkyl having from about 1 to about 20 carbon atoms;

(b) from about 0.1% to about 10% of a sunscreen compound (II) having the general structure



wherein D and E are substituents independently selected from the group consisting of H, straight or branched chain alkyl having from about 1 to about 20 carbon atoms, and -OR, wherein R is H, or straight or branched chain alkyl having from about 1 to about 20 carbon atoms;

(c) from about 0.1% to about 25% of a physical sunblock; and

(d) a pharmaceutically-acceptable carrier;

wherein the weight ratio of sunscreen compound (I) to sunscreen compound (II) is from about 1:1.5 to about 1.5:1.

The present invention also relates to methods for protecting the skin of humans or lower animals from the effects of UVA and UVB wavelength radiation.

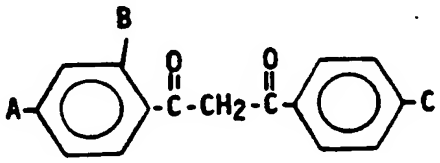
All percentages and ratios used herein are by weight of the total composition and all measurements made at 25°C, unless otherwise designated.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of the instant invention comprise the following essential as well as optional components.

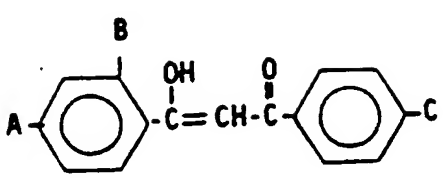
Dibenzoylmethane Sunscreen Compound

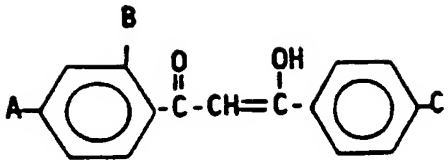
A UVA-absorbing dibenzoylmethane sunscreen compound is an essential component of the present invention. This sunscreen compound has the general structure



wherein A is a substituent selected from the group consisting of H, -OR, and $-NR_2$ wherein each R is independently H, or straight or branched chain alkyl having from about 1 to about 20 carbon atoms; B is a substituent selected from the group consisting of H and -OH; and C is a substituent selected from the group consisting of H, or straight or branched chain alkyl having from about 1 to about 20 carbon atoms.

Even though the dibenzoylmethane chromophore is represented as a 1,3-diketone it should be understood that this representation in no way excludes other tautomeric forms of the functional group such as the enol form. Thus whenever the 1,3-diketone form is designated, it is understood that all appropriate enol tautomers are also contemplated and included herein. These tautomeric enol forms of the dibenzoylmethane chromophore can be represented by the following tautomeric structures.





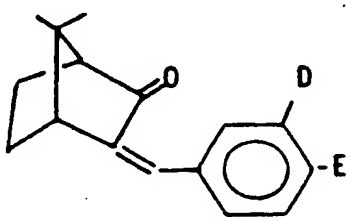
Dibenzoylmethane susncreen agents are described in U.S. Patent No. 4,489,057, to Welters et al., issued December 18, 1984, and U.S. Patent No. 4,387,089, to DePolo, issued June 7, 1983, both of which are incorporated by reference herein. See also, Sunscreens: Development, Evaluation, and Regulatory Aspects, edited by N.J. Lowe and N.A. Shaath, Marcel Dekker, Inc. (1990), which is incorporated by reference herein in its entirety. Examples of dibenzoylmethane susncreens useful herein include those selected from the group consisting of 4,4'-methoxy-t-butyldibenzoylmethane, 4-isopropyldibenzoylmethane, 4-methoxydibenzoylmethane, 2,4'-hydroxy-t-butyldibenzoylmethane, 2,4,4'-hydroxymethoxy-t-butyldibenzoylmethane, and mixtures thereof. More preferred are 4,4'-methoxy-t-butyldibenzoylmethane, 4-isopropyldibenzoylmethane, and mixtures thereof.

The sunscreen 4,4'-methoxy-t-butyldibenzoylmethane, which is also known as butyl methoxydibenzoylmethane, is commercially available under the trademark Parsol^{R} 1789 from Givaudan. See CTFA International Cosmetic Ingredient Dictionary, fourth edition, 1991, pp. 68-69, which is incorporated by reference herein. The sunscreen 4-isopropyldibenzoylmethane, which is also known as isopropyl dibenzoylmethane, is commercially available under the trademark Eusolex^{R} 8020 from Merck. See CTFA International Cosmetic Ingredient Dictionary, fourth edition, 1991, p. 267, which is incorporated by reference herein.

The dibenzoylmethane sunscreen compound of the instant invention is present from about 0.1% to about 10%, preferably from about 1% to about 5%, and most preferably from about 1.5% to about 2.5%.

Benzylidene Camphor Sunscreen Compound

A UVB-absorbing benzylidene camphor sunscreen compound is an essential component of the present invention. This sunscreen compound has the general structure



wherein D and E are substituents independently selected from the group consisting of H, straight or branched chain alkyl having from about 1 to about 20 carbon atoms, and -OR, where R is H, or straight or branched chain alkyl having from about 1 to about 20 carbon atoms. The camphor moiety of these susncreens can be derived from either D-camphor, L-camphor, or racemic D,L-camphor. U.S. Patent No. 3,781,417, to Welters et al., issued December 25, 1973, which is incorporated by reference herein, describes benzylidene camphor sunscreen compounds. See also, Sunscreens: Development, Evaluation, and Regulatory Aspects, edited by N.J. Lowe and N.A. Shaath, Marcel Dekker, Inc. (1990), which is incorporated by reference herein in its entirety. Examples of benzylidene camphor susncreens useful herein include those selected from the group consisting of 3-(4-methylbenzylidene) camphor, 3-benzylidene camphor, 3-(4-methoxybenzylidene) camphor, and mixtures thereof. More preferred are 3-(4-methylbenzylidene) camphor, 3-benzylidene camphor, and mixtures thereof. Most preferred is 3-(4-methylbenzylidene) camphor.

The sunscreen 3-(4-methylbenzylidene) camphor, which is also known as 4-methylbenzylidene camphor, is commercially available under the trademark Eusolex^{R} 6300 from Merck and also from Rona. See CTFA International Cosmetic Ingredient Dictionary, fourth edition, 1991, pp. 317-318, which is incorporated by reference herein.

The benzylidene camphor sunscreen compound of the instant invention is present from about 0.1% to about 10%, preferably from about 1% to about 5%, and most preferably from about 1.5% to about 2.5%.

Ratio of Sunscreens

The weight ratio of UVA-absorbing dibenzoyl methane sunscreen to UVB-absorbing benzylidene camphor sunscreen is an important criticality of the present invention. The weight ratio of dibenzoyl methane sunscreen to benzylidene camphor sunscreen is from about 1:1.5 to about 1.5:1, preferably from about 1:1.25 to about 1.25:1, more preferably from about 1:1.1 to about 1.1:1, and most preferably about 1:1.

Physical Sunblocks

In highly preferred embodiments of the present invention, the compositions comprise an inorganic physical sunblock. Without being limited by theory, it is believed that the physical sunblock helps to provide more uniform coverage across the UVA and UVB regions.

Inorganic physical sunblocks useful herein include those selected from the group consisting of titanium dioxide, iron oxides, zinc oxide, silica, mica, and mixtures thereof. More preferred are those selected from the group consisting of titanium dioxide, iron oxides, and zinc oxide. Most preferred is titanium dioxide.

Titanium dioxide, iron oxides, zinc oxide, silica, and mica are described in CTFA International Cosmetic Ingredient Dictionary, Fourth Edition (1991), pp. 257-259, 324-326, 528-529, 611-612, and 649, which are incorporated by reference herein.

When titanium dioxide is selected as a physical sunblock for use herein, the titanium dioxide can have an anatase, rutile, or amorphous structure. The titanium dioxide preferably has a mean particle size from about 1 nm to about 100 nm, more preferably from about 15 nm to about 50 nm, and most preferably from about 30 nm to about 50 nm. The titanium

dioxide particles can be uncoated or can be coated with a variety of materials including, but not limited to, amino acids; aluminum compounds such as alumina, aluminum stearate, aluminum laurate and the like; carboxylic acids and their salts, e.g., stearic acid and its salts; phospholipids such as lecithin; organic silicone compounds; inorganic silicon compounds such as silica, silicates; and mixtures thereof. Various grades and forms of titanium dioxide are described in CTFA International Cosmetic Ingredient Dictionary, Fourth Edition (1991), pp. 318-319; U.S. Patent No. 4,820,508 to Wortzman, issued April 11, 1989; and World Patent No. WO 90/11067 to Elsom et al., published October 4, 1990; these three references are incorporated by reference herein in their entirety. See also, Sunscreens: Development, Evaluation, and Regulatory Aspects, edited by N.J. Lowe and N.A. Shaath, Marcel Dekker, Inc. (1990), which is incorporated by reference herein in its entirety.

Suitable grades of titanium dioxide for use in the compositions of the present invention are available commercially such as the MT micronized series distributed by Tri-K Industries (Emerson, NJ), and manufactured by Tayca (Japan). These micronized titanium dioxides generally have a mean primary particle size ranging from about 10 nm to about 50 nm. For example, titanium dioxide having a mean primary particle size of about 15 nm is available under the trade designations MT-150W (uncoated) and MT-100T (coated with stearic acid and aluminum compounds). Uncoated titanium dioxides having mean primary particle sizes of around 35 nm and around 50 nm are available under the trade designations MT-500B and MT-600B, respectively. A titanium dioxide having a mean primary particle size of around 35 nm and coated with stearic acid, alumina, and silica is available under the trade name designation MT-500SA. Other coated titanium dioxides include MT-100F (modified with stearic acid and iron hydroxide and having a mean primary particle size around 15 nm), and MT-100S (treated with lauric acid and aluminum hydroxide and having a

mean primary particle size around 15 nm). Mixtures of two or more types and particle size variations of titanium dioxide can be used in the present invention.

The titanium dioxide is present from about 0.1% to about 25% of the weight of the total composition, more preferably from about 0.5% to about 5%, and most preferably from about 1% to about 4%.

Pharmaceutically-Acceptable Carrier

The compositions of the instant invention comprise as a necessary component a safe and effective amount of a pharmaceutically-acceptable carrier which can be of a variety of different forms. By "pharmaceutically-acceptable" is meant that the carrier comprises common pharmaceutical and cosmetic ingredients which are typically used in the industry and which are generally recognized as safe for human contact. The topical carrier can be in the form of an emulsion including, but not limited to, oil-in-water, water-in-oil, water-in-oil-in-water, and oil-in-water-in-silicone emulsions. These emulsions can cover a broad range of consistencies including thin lotions (which can also be suitable for spray or aerosol delivery), creamy lotions, light creams, heavy creams, and the like. Other suitable topical carriers include anhydrous liquid solvents such as oils and alcohols; aqueous-based single phase liquid solvents (e.g. hydro-alcoholic solvent systems); anhydrous solids and semisolids (such as gels and sticks); and aqueous based gel and mousse systems. Examples of topical carrier systems useful in the present invention are described in the following four references all of which are incorporated herein by reference in their entirety: "Sun Products Formulary" Cosmetics & Toiletries, vol. 105, pp. 122-139 (December 1990); "Sun Products Formulary", Cosmetics & Toiletries, vol. 102, pp. 117-136 (March 1987); U.S. Patent No. 4,960,764 to Figueroa et al., issued October 2, 1990; and U.S. Patent No. 4,254,105 to Fukuda et al., issued March 3, 1981.

The pharmaceutically-acceptable topical carriers, in total, typically comprise from about 0.1% to about 99.8% by weight of the sunscreen compositions of the present invention, preferably from about 80% to about 99%, and most preferably from about 85% to about 95%.

A preferred topical carrier of the compositions of the instant invention is an oil-in-water type emulsion.

Optional Components

Emulsifiers

An optional component of the compositions of the instant invention is an emulsifier. Suitable emulsifiers can include any of a wide variety of nonionic, cationic, anionic, and zwitterionic emulsifiers disclosed in the prior patents and other references. See McCutcheon's, Detergents and Emulsifiers, North American Edition (1986), published by Allured Publishing Corporation; U.S. Patent No. 5,011,681 to Ciotti et al., issued April 30, 1991; U.S. Patent No. 4,421,769 to Dixon et al., issued December 20, 1983; and U.S. Patent No. 3,755,560 to Dickert et al., issued August 28, 1973; these four references are incorporated herein by reference in their entirety.

Suitable emulsifier types include esters of glycerin, esters of propylene glycol, fatty acid esters of polyethylene glycol, fatty acid esters of polypropylene glycol, esters of sorbitol, esters of sorbitan anhydrides, carboxylic acid copolymers, esters and ethers of glucose, ethoxylated ethers, ethoxylated alcohols, alkyl phosphates, polyoxyethylene fatty ether phosphates, fatty acid amides, acyl lactylates, soaps and mixtures thereof.

Suitable emulsifiers can include, but are not limited to, polyethylene glycol 20 sorbitan monolaurate (Polysorbate 20), polyethylene glycol 5 soya sterol, Steareth-20, Ceteareth-20, PPG-20 methyl glucose ether distearate, Ceteth-10, Polysorbate 80, cetyl phosphate, potassium dicetyl/cetyl phosphate, diethanolamine dicetyl/cetyl phosphate, triethanolamine dicetyl/

cetyl phosphate, tromethamine dicetyl/cetyl phosphate, Polysorbate 60, glyceryl stearate, PEG-100 stearate, and mixtures thereof.

The emulsifiers can be used individually or as a mixture of two or more and comprise from about 0.1% to about 10%, preferably from about 1% to about 7%, and most preferably from about 1% to about 5% of the compositions of the present invention.

Humectants/Moisturizers/Skin Conditioners

A highly preferred optional component of the compositions of the instant invention is at least one humectant/moisturizer/skin conditioner. A variety of these materials can be employed and each can be present at a level of from about 0.1% to about 20%, more preferably from about 0.5% to about 10% and most preferably from about 1% to about 5%. These materials include urea; guanidine; glycolic acid and glycolate salts (e.g. ammonium and quaternary alkyl ammonium); lactic acid and lactate salts (e.g. ammonium and quaternary alkyl ammonium); aloe vera in any of its variety of forms (e.g., aloe vera gel); polyhydroxy alcohols such as sorbitol, glycerol, hexanetriol, propylene glycol, butylene glycol, hexylene glycol and the like; polyethylene glycol; sugars and starches; sugar and starch derivatives (e.g., alkoxylated glucose); hyaluronic acid; lactamide monoethanolamine; acetamide monoethanolamine; and mixtures thereof.

Preferred humectants/moisturizers/skin conditioners useful in the compositions of the methods of the present invention are the C_3-C_6 diols and triols, and also aloe vera gel. Especially preferred is the triol, glycerol, and also aloe vera gel.

Carboxylic Acid Copolymers

Another optional component of the compositions of the instant invention is a carboxylic copolymer (acrylic acid copolymer). These materials are known as carbomers and are available under the Carbopol^R trademark from B.F. Goodrich). Also useful are the acrylate/alkyl acrylate crosspolymers such as Acrylates/C10-C30 Alkyl Acrylate Crosspolymer (available as

Pemulen TR-1, Pemulen TR-2, and Carbopol 1342 from B.F. Goodrich). These polymers are more fully described in U.S. Patent No. 4,509,949, to Huang et al., issued April 5, 1985; U.S. Patent No. 2,798,053, to Brown, issued July 2, 1957; and CTFA International Cosmetic Ingredient Dictionary, fourth edition, 1991, pp. 12 and 80; these references are all incorporated herein by reference in their entirety.

These polymers comprise from about 0.025% to about 0.75%, preferably from about 0.05% to about 0.50% and most preferably from about 0.10% to about 0.50% of the compositions useful herein.

Emollients

The compositions of the present invention can also optionally comprise at least one emollient. Examples of suitable emollients include, but are not limited to, volatile and non-volatile silicone oils (e.g., dimethicone, cyclomethicone, dimethiconol, and the like), highly branched hydrocarbons, and non-polar carboxylic acid and alcohol esters, and mixtures thereof. Emollients useful in the instant invention are further described in U.S. Patent No. 4,919,934, to Deckner et al., issued April 24 1990, which is incorporated herein by reference in its entirety.

The emollients can typically comprise in total from about 0.5% to about 50%, preferably from about 0.5% to about 25%, and more preferably from about 0.5% to about 10% by weight of the compositions useful in the present invention.

Optional Components

A variety of additional ingredients can be incorporated into the compositions useful in the present invention.

The compositions can optionally comprise additional sunscreens. When used, additional sunscreens can comprise from about 0.1% to about 20% of the compositions useful herein. Exact amounts will vary depending upon the sunscreen chosen and the desired Sun Protection Factor (SPF). SPF is a commonly

used measure of photoprotection of a sunscreen against erythema. See Federal Register, Vol. 43, No. 166, pp. 38206-38269, August 25, 1978, which is incorporated herein by reference in its entirety.

Non-limiting examples of other additional ingredients include other vitamins and derivatives thereof (e.g., ascorbic acid, vitamin E, tocopheryl acetate, retinoic acid, retinol, retinoids, and the like); thickening agents (e.g. polyacrylamide and C_{13-14} isoparaffin and laureth-7, available as Sepigel from Seppic Corporation); resins; gums; cationic polymers and thickeners (e.g., cationic guar gum derivatives such as guar hydroxypropyltrimonium chloride and hydroxypropyl guar hydroxypropyltrimonium chloride, available as the Jaguar C series from Rhone-Poulenc; copolymers of acrylamide and a cationic acrylate (available as Salcare SC92 from Allied Colloid); polymers for aiding the film-forming properties and substantivity of the composition (such as a copolymer of eicosene and vinyl pyrrolidone, an example of which is available from GAF Chemical Corporation as Ganex V-220^R); preservatives for maintaining the antimicrobial integrity of the compositions; skin penetration aids such as DMSO, 1-dodecylazacycloheptan-2-one (available as Azone from the Upjohn Co.) and the like; anti-acne medicaments (resorcinol, salicylic acid, erythromycin, benzoyl peroxide, and the like); artificial tanning agents such as dihydroxyacetone and the like; skin bleaching (or lightening) agents including but not limited to hydroquinone, ascorbic acid, kojic acid and sodium metabisulfite; antioxidants; chelators and sequestrants; and aesthetic components such as fragrances, pigments, colorings, essential oils, skin sensates, astringents, skin soothing agents, skin healing agents and the like, nonlimiting examples of these aesthetic components include clove oil, menthol, camphor, eucalyptus oil, eugenol, menthyl lactate, witch hazel distillate, allantoin, bisabalol, dipotassium glycyrrhizinate and the like.

Methods for Protecting and Moisturizing the Skin

The compositions of the present invention are useful for the protection of the skin from the harmful effects of UVA and UVB radiation. These compositions can also be used to help mositurize the skin. Typically, these compositions are applied to the skin in an effective amount, which is about 2 mg/cm^2. These compositions can be used on a regular or daily basis.

EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention.

Ingredients are identified by chemical or CTFA name.

EXAMPLES I-V

Daily Moisturizing Lotions Containing Sunscreens

The following ingredients are combined to form an oil-in-water emulsion using conventional mixing techniques.

	% Weight				
Ingredients	I	II	III	IV	V
Water	QS100	QS100	QS100	QS100	QS100
Acrylates/C10-30 Alkyl Acrylate Crosspolymer	0.125	0.125	0.125	0.125	0.125
Disodium EDTA	0.05	0.05	0.05	0.05	0.05
Carbomer 954	0.20	0.20	0.20	0.20	0.20
Glycerin	1.00	1.00	1.00	1.00	1.00
Hexylene Glycol	2.00	2.00	2.00	2.00	2.00
Methylparaben	0.25	0.25	0.25	0.25	0.25
Dimethicone (and) Cyclomethicone[1]	0.75	0.75	0.75	0.75	0.75
PEG-10 Soya Sterol	0.10	0.10	0.10	0.10	0.10
Stearic Acid	1.00	1.00	1.00	1.00	1.00

	Cetyl Alcohol	1.00	1.00	1.00	1.00	1.00
	Cetyl Palmitate	0.50	0.50	0.50	0.50	0.50
	DEA Cetyl Phosphate	0.75	0.75	0.75	0.75	0.75
	Castor Oil	0.05	0.05	0.05	0.05	0.05
	Aluminum Starch Octenylsuccinate	0.50	0.50	0.50	0.50	0.50
	Ethylparaben	0.15	0.15	0.15	0.15	0.15
	Butyl Methoxydibenzoylmethane	1.50	1.50	2.00	1.90	1.45
	4-Methylbenzylidene Camphor	1.50	1.50	2.00	2.00	1.50
	C12-15 Alkyl Benzoate	10.0	10.0	10.0	10.0	10.0
	PVP/Eicosene Copolymer	0.50	0.50	0.50	0.50	0.50
	Titanium Dioxide[2]	1.50	1.50	2.00	--	--
	Titanium Dioxide Coated[3]	--	--	--	1.50	1.50
	Zinc Oxide[4]	0.80	--	--	--	0.25
	Iron Oxide	--	--	--	--	0.25
	Triethanolamine (99%)	0.73	0.73	0.73	0.73	0.73
	Benzyl Alcohol	0.30	0.30	0.30	0.30	0.30

[1]Available as Dow Corning 200/350 Fluid.

[2]Available as MT-500B and/or MT-600B from Tri-K Industries Inc., Emerson, N.J.

[3]Available as MT-500SA (coated wtih stearic acid, alumina, and silica) from Tri-K Industries.

[4]Available as a suspension in octyl palmitate from Tioxide Corp.

The resulting emulsion is useful for topical application to the skin as a daily moisturizer and to provide protection from the harmful effects of ultraviolet radiation.

EXAMPLE VI

Sunscreen Oil

A sunscreen oil is prepared by combining the following components utilizing conventional mixing techniques.

Ingredients	% Weight
Mineral Oil	QS100
Butyl Methoxydibenzoylmethane	3.00
4-Methylbenzylidene Camphor	3.00
C_{12-15} Alcohols Benzoate	15.00
Isopropyl Myristate	2.00
Sorbitan Oleate	1.50
Propylparaben	0.50
D&C Red #17	0.002

The above ingredients are combined and heated until the propylparaben is dissolved.

This sunscreen oil is useful for topical application to the skin to provide protection from the harmful effects of ultraviolet radiation.

EXAMPLE VII

Anhydrous Sunscreen Gel

An anhydrous sunscreen gel is prepared by combining the following components utilizing conventional mixing techniques.

Ingredients	% Weight
Mineral Oil	QS100
Butyl Methoxydibenzoylmethane	2.45
4-Methylbenzylidene Camphor	2.50
Titanium Dioxide	0.50
Petrolatum	15.00
Paraffin Wax	10.00
Ozokerite	8.00
Isopropyl Myristate	5.00
Fragrance	0.50
D&C Yellow #10 Aluminum Lake and Mineral Oil and Petrolatum[1]	0.545
D&C Red #17	0.0055
Propylparaben	0.100
C_{12-15} Alcohols Benzoate	10.00
Butylparaben	0.03

[1]Available as Opatint Yellow OD-2169 from Colorcon.

The above ingredients are combined and heated with mixing until dispersed.

This anhydrous sunscreen gel is useful for topical application to the skin to provide protection from the harmful effects of ultraviolet radiation.

EXAMPLE VIII

Hydroalcoholic Sunscreen Gel

A hydroalcoholic sunscreen gel is prepared by combining the following components utilizing conventional mixing techniques.

Ingredients	% Weight
Phase A	
Water	QS100
Hydroxyethyl cellulose	0.90
TEA-Coco-Hydrolyzed Animal Protein	2.00
Hydrolyzed Animal Collagen[1]	1.00
Butyl Methoxydibenzoylmethane	1.50
4-Methylbenzylidene Camphor	1.50
Titanium Dioxide	0.10
Glycerin	1.00
Phase B	
Soluble Animal Collagen[1]	3.00
Phase C	
Alcohol SD-40	20.00
Polysorbate 20	0.80
Fragrance	0.50

[1]Available as Polypro 5000 from Geo. A. Hormel & Co.

[2]Available as Sollagen from Geo. A. Hormel & Co.

Heat water to 60-65°C and sprinkle the hydroxyethyl cellulose into the stirred water. Allow to fully dissolve to a clear solution. Stop heating and add remaining Phase A ingredients. Cool to below 35°C and add Phase B. Mix Phase C ingredients and add to the mixture of Phases A and B.

This hydroalcoholic gel is useful for topical application to the skin to provide protection from the harmful effects of ultraviolet radiation.

EXAMPLE IX

Lip Protecting Stick

A lip protecting stick is prepared by combining the following components utilizing conventional mixing techniques.

Ingredients	% Weight
Mineral Oil	QS100
Butyl Methoxydibenzoylmethane	2.50
4-Methylbenzylidene Camphor	2.50
Titanium Dioxide	1.00
Petrolatum	15.94
C_{12-15} Alcohols Benzoate	13.00
Ozokerite Wax	13.00
Candililla Wax	13.00
Oleyl Alcohol	8.00
Tocopheryl Acetate	1.00
Propylparaben	0.10

The ingredients are combined together and heated with mixing until uniform, and the resulting mixture is poured into appropriate containers and allowed to harden.

This lip protecting stick is useful for topical application to the lips to provide protection from the harmful effects of ultraviolet radiation.

EXAMPLE X

Sunscreen Spray Emulsion Lotion

A sunscreen spray emulsion is prepared by combining the following components utilizing conventional mixing techniques.

Ingredients	% Weight
Phase A	
Water	QS100
Carbomer 1342	0.10
Disodium EDTA	0.10
Phase B	
Butyl Methoxydibenzoylmethane	2.40
4-Methylbenzylidene Camphor	2.50
Titanium Dioxide	0.10

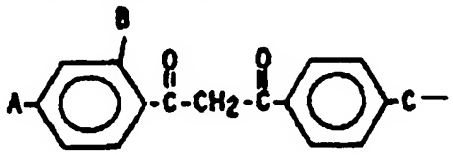
PVP Eicosene Copolymer	1.00
Stearic Acid	0.15
Simethicone	0.01
Stearoxy Dimethicone	0.50
C_{12-15} Alcohols Benzoate	10.00
Phase C	
Water	2.00
Triethanolamine (99%)	0.175
Phase D	
Water	2.00
Butylene Glycol	2.00
DMDM Hydantoin (and) Iodopropynyl Butylcarbamate	0.25
Dexpanthenol	0.50
Phase E	
Fragrance	0.30
Cyclomethicone	2.00

This sunscreen spray emulsion is useful for topical application to the skin to provide protection from the harmful effects of ultraviolet radiation.

WHAT IS CLAIMED IS:

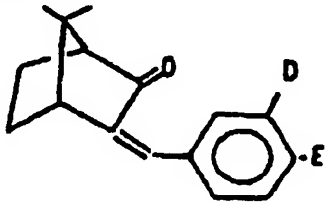
1. A sunscreen composition having improved photostability and broad UVA and UVB coverage, comprising:

(a) from 0.1% to 10% of a sunscreen compound (I) having the general structure



wherein A is a substituent selected from the group consisting of H, -OR, and -NR_2 wherein each R is independently H, or straight or branched chain alkyl having from 1 to 20 carbon atoms; B is a substituent selected from the group consisting of H and -OH; and C is a substituent selected from the group consisting of H, or straight or branched chain alkyl having from 1 to 20 carbon atoms;

(b) from 0.1% to 10% of a sunscreen compound (II) having the general structure



wherein D and E are substituents independently selected from the group consisting of H, straight or branched chain alkyl having from 1 to 20 carbon atoms, and -OR, where R is H, or straight or branched chain alkyl having from 1 to 20 carbon atoms;

(c) from 0.1% to 25% of a physical sunblock; and

(d) a safe and effective amount of a pharmaceutically-acceptable carrier;

wherein the weight ratio of sunscreen compound (I) to sunscreen compound (II) is from 1:1.5 to 1.5:1.

2. A sunscreen composition according to Claim 1 comprising from 0.5% to 5% of sunscreen compound (I); from 0.5% to 5% of sunscreen compound (II); and from 1% to 4% of a physical sunblock.

3. A sunscreen composition according to Claim 2 wherein the weight ratio of sunscreen compound (I) to sunscreen compound (II) is from 1:1.1 to 1.1:1, preferably wherein the weight ratio of sunscreen compound (I) to sunscreen compound (II) is 1:1.

4. A sunscreen composition according to Claim 3 wherein sunscreen compound (I) is selected from the group consisting of 4,4'-methoxy-t-butyldibenzoylmethane, 4-isopropyldibenzoylmethane, 4-methoxydibenzoylmethane, 2,4'-hydroxy-t-butyldibenzoylmethane, 2,4,4'-hydroxy-methoxy-t-butyldibenzoylmethane, and mixtures thereof; sunscreen compound (II) is selected from the group consisting of 3-(4-methylbenzylidene) camphor, 3-benzylidene camphor, 3-(4-methoxybenzylidene) camphor, and mixtures thereof; and said physical sunblock is selected from the group consisting of titanium dioxide, iron oxides, zinc oxide, silica, mica, and mixtures thereof; preferably wherein sunscreen compound (I) is selected from the group consisting of 4,4'-methoxy-t-butyldibenzoylmethane, 4-isopropyldibenzoylmethane, and mixtures thereof; sunscreen compound (II) is 3-(4-methylbenzylidene) camphor; and said physical sunblock is selected from the group consisting of titanium dioxide, iron oxides, zinc oxide, and mixtures thereof; and more preferably wherein sunscreen compound (I) is selected from the group

consisting of 4,4'-methoxy-t-butyldibenzoyl- methane, 4-isopropyldibenzoylmethane, and mixtures thereof; sunscreen compound (II) is 3-(4-methylbenzylidene) camphor; and said physical sunblock is titanium dioxide.

5. A sunscreen composition according to Claim 1 wherein said physical sunblock has been surface treated; preferably wherein said physical sunblock is selected from titanium dioxide which has been surface treated with a mixture of stearic acid, alumina, and silica.

6. A sunscreen composition according to Claim 1 wherein said composition further comprises from 0.1% to 20% of a sunscreen compound selected from the group consisting of 2-ethylhexyl p-methoxycinnamate, 2-ethylhexyl N,N-dimethyl-p-aminobenzoate, p-aminobenzoic acid, octocrylene, 2-phenylbenzimidozole-5-sulfonic acid, oxybenzone, homomenthyl salicylate, octyl salicylate, sulisobenzone, amyl p-methoxy- cinnamate, amyl N,N-dimethyl-p-aminobenzoate, 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester of 2,4-dihydroxybenzophenone; N,N-di-(2-ethylhexyl)-4-aminobenzoic acid ester with 4-hydroxydibenzoylmethane; 4-N,N(2-ethylhexyl)methylaminobenzoic acid ester with 4-hydroxydibenzoylmethane; 4-N,N-(2-ethylhexyl)methylaminobenzoic acid ester of 2-hydroxy-4-(2-hydroxyethoxy)benzophenone; 4-N,N-(2-ethylhexyl) methylaminobenzoic acid ester of 4-(2-hydroxyethoxy)dibenzoylmethane; N-N-di-(2-ethylhexyl)-4-aminobenzoic acid ester of 2-hydroxy-4-(2-hydroxyethoxy)benzophenone, and N,N-di-(2-ethylhexyl)-4-aminobenzoic acid ester of 4-(2-hydroxyethoxy)-dibenzoylmethane, and mixtures thereof.

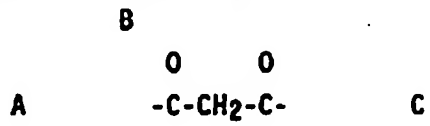
7. A sunscreen composition according to Claim 1 or Claim 4 wherein said pharmaceutically-acceptable carrier is an oil-in-water emulsion.

8. A sunscreen composition according to Claim 7 which further comprises glycerol, a silicone fluid, a carboxylic acid copolymer, and DEA-cetylphosphate.

9. A sunscreen composition according to Claim 1 wherein said pharmaceutically-acceptable carrier is selected from the group consisting of a water-in-oil emulsion, an oil, an aqueous-based lotion or gel, and an anhydrous gel.

10. The use of a composition in the manufacture of a medicament for protecting the skin of humans or lower animals from the effects of UVA and UVB wavelength radiation, said composition comprising:

(a) from 0.1% to 10% of a sunscreen compound (I) having the general structure



wherein A is a substituent selected from the group consisting of H, -OR, and $-NR_2$ wherein each R is independently H, or straight or branched chain alkyl having from 1 to 20 carbon atoms; B is a substituent selected from the group consisting of H and -OH; and C is a substituent selected from the group consisting of H, or straight or branched chain alkyl having from 1 to 20 carbon atoms;

(b) from 0.1% to 10% of a sunscreen compound (II) having the general structure

D

E

wherein D and E are substituents independently selected from the group consisting of H, straight or branched chain alkyl having from 1 to 20 carbon atoms, and -OR, where R is H, or straight or branched chain alkyl having from 1 to 20 carbon atoms;

(c) from 0.1% to 25% of a physical sunblock; and

(d) a safe and effective amount of a pharmaceutically-acceptable carrier;

wherein the weight ratio of sunscreen compound (I) to sunscreen compound (II) is from 1:1.5 to 1.5:1.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/06897

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 A61K7/42

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	A61K

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	EP,A,0 431 755 (UNILEVER PLC.) 12 June 1991 see the whole document	1-4,6-10
P,X	EP,A,0 521 651 (UNILEVER PLC.) 7 January 1993 see the whole document	1-4,6-10
A	GB,A,2 198 944 (L'OREAL) 29 June 1988 see the whole document	1-10
A	EP,A,0 303 995 (KAO CORPORATION) 22 February 1989 see the whole document	1-10
A	EP,A,0 154 928 (KAO CORPORATION) 18 September 1985 see the whole document	1-10

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
14 OCTOBER 1993	22. 10 93.
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	COUCKUYT P.J.R.

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9306897
SA 77338

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 14/10/93

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0431755	12-06-91	AU-B-	628232	10-09-92
		AU-A-	6591090	16-05-91
		JP-A-	3170416	24-07-91
		US-A-	5152983	06-10-92
EP-A-0521651	07-01-93	AU-A-	1937792	07-01-93
		JP-A-	5186322	27-07-93
GB-A-2198944	29-06-88	LU-A-	86703	14-07-88
		AU-B-	611871	27-06-91
		AU-A-	8213687	09-06-88
		BE-A-	1000623	21-02-89
		CH-A-	674145	15-05-90
		DE-A-	3741420	09-06-88
		FR-A-	2607700	10-06-88
		JP-A-	63215619	08-09-88
		NL-A-	8702954	01-07-88
EP-A-0303995	22-02-89	JP-A-	1048881	23-02-89
EP-A-0154928	18-09-85	JP-C-	1464239	28-10-88
		JP-A-	60190708	28-09-85
		JP-B-	63006526	10-02-88
		US-A-	4710373	01-12-87

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82